Enhancement and depression in second-order optical nonlinearity of Ba2TiGe208 in crystallized glass prepared in a high magnetic field

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Enhancement and depression in second-order optical nonlinearity of $Ba_2TiGe_2O_8$ in crystallized glass prepared in a high magnetic field

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A magnetic field of $H=10$ T was applied perpendicularly or parallel to the surface of the $30BaO.15TiO_2.55GeO_2$ (BTG) glass during its crystallization, and the effect of the magnetic field on the crystal orientation and second-order optical nonlinearity of the $Ba_2TiGe_2O_8$ crystals formed at the glass surface was examined. Compared with the sample prepared by conventional crystallization in zero magnetic field, the *c*-axis (polarization axis) orientation and second-harmonic intensity of the $Ba_2TiGe_2O_8$ crystals at the surface were enhanced in the sample fabricated with the field perpendicular to the surface and, by contrast, were depressed in the sample fabricated with the field parallel to the surface. The present study indicates that the application of high magnetic fields during crystallization is a technique to control the crystal orientations and optical properties of BTG crystallized glasses. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2170412]

I. INTRODUCTION

In the area of photonics, transparent crystallized glasses consisting of nonlinear optical/ferroelectric crystals have received much attention, because such materials have a high potential for applications in laser hosts, tunable waveguides, tunable fiber gratings, and so on. For instance, crystallized glasses consisting of $LaBGeO_5$, $SrBi_2Ta_2O_9$, and $Ba_2TiGe_2O_8$, which are optical nonlinear/ferroelectric crystals, have been fabricated.[1–4] Since nonlinear optical/ferroelectric crystals have crystallographic anisotropies giving anisotropic polar directions, it is of importance to control crystal orientations for the fabrication of photonic materials with desired properties. Tamagawa *et al.*[5] found that the second-harmonic (SH) intensity of nanocrystallized TeO_2-based glasses is enhanced by applications of thermal poling. Recently, it has been recognized that the use of high magnetic fields is effective in enhancing orientations of nonmagnetic crystals.[6–8] Indeed, the present authors' group[9] applied a high magnetic field of 10 T in the crystallization process of $Bi_2Sr_2CaCu_2O_x$ superconducting precursor glasses and found that superconducting crystal grains with a platelike shape tend to stack (i.e., *c*-axis orientation) to the direction of the magnetic field, giving better superconducting properties compared with the samples crystallized in a normal heat treatment with zero magnetic field. There has been, however, no report on the effect of the application of high magnetic fields on the formation and orientation of nonlinear/ferroelectric crystals in glass and on optical properties of crystallized glasses.

In this study, we applied a magnetic field of 10 T in the crystallization of the $30BaO.15TiO_2.55GeO_2$ glass and examined whether the application of such a high magnetic field has the effect on the crystal orientation and second-order optical nonlinearity of the $Ba_2TiGe_2O_8$ crystals formed at the glass surface. It should be pointed out that transparent surface-crystallized glasses consisting of $Ba_2TiGe_2O_8$ crystals are good candidates for tunable light control devices because of their large second-order optical nonlinearities.[3,4]

II. EXPERIMENT

The glass composition used in this study was $30BaO.15TiO_2.55GeO_2$ (mol %). Details of the glass preparation method have been described elsewhere.[3,4] Glass transition, T_g, crystallization onset, T_x, and crystallization peak, T_p, temperatures of the glass sample were determined using differential thermal analyses (DTAs) at a heating rate of 10 K/min in air. The DTA pattern for the $30BaO.15TiO_2.55GeO_2$ glass (bulk shape) has been shown in previous paper.[10] The quenched glasses were annealed at T_g to release internal stress and then polished mechanically to a mirror finish with CeO_2 powders. The well-polished glass plates with a thickness of about 1 mm were placed in a superconducting magnet (TM-10VH10, Toshiba) and heat treated at temperatures under the presence of the magnetic field of 10 T, i.e., $H=10$ T. After heat treatment, the samples were cooled in the furnace to room temperature. The directions of the application of $H=10$ T were perpendicular or parallel to the surface of the glass plates. For comparison, other crystallized glasses were also prepared using the same furnace and processing, but in zero magnetic field.

The crystalline phase present in the heat-treated samples was identified by x-ray-diffraction (XRD) analyses (Cu $K\alpha$ radiation) at room temperature. Microstructures in the heat-treated samples were examined using a scanning electron microscopy (SEM). Refractive indices of the heat-treated samples in the wavelength range of $\lambda=288.6-1654.4$ nm were measured at room temperature using an ellipsometer

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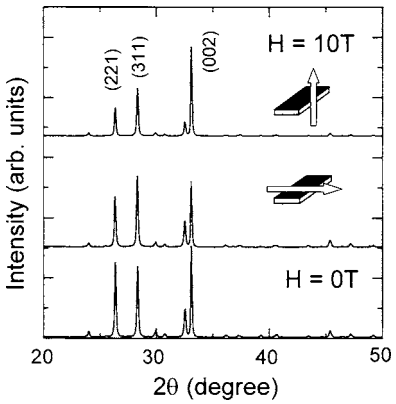

FIG. 1. XRD patterns at room temperature for the surface of the crystallized glasses obtained by heat treatment at 720° C for 3 h in the magnetic field (H=10 T) and zero magnetic field (H=0 T). The peaks are assigned to $Ba_2TiGe_2O_8$ crystals.

(UVISEL-2617K, Jobin Yvon). The refractive indices at λ =1064 and 532 nm were estimated with the following Wemple's equation;[11,12]

$$n^2 = 1 + \frac{k\lambda^2}{\lambda^2 - \lambda_0^2}, \tag{1}$$

where n is the refractive index at a given wavelength λ. k and λ_0 are the calculated parameters. The SH intensities of the heat-treated samples were evaluated by Maker fringe techniques.[13,14] A fundamental wavelength of a Q-switched Nd^{3+}: yttrium-aluminum-garnet (YAG) laser operating at λ =1064 nm was used as the incident right, and the intensities of green light [λ=532 nm, second-harmonic generation (SHG)] emissions were measured. As polarization for SH intensity measurements, the combination of p excitation and p detection (pp polarization) was used. A z-cut α-quartz single crystal with a thickness of 0.6 mm was used as a reference, i.e., its value of the second-order optical nonlinearity is d_{11}=0.503 pm/V.[15]

III. RESULTS AND DISCUSSION

The composition of $30BaO.15TiO_2.55GeO_2$ is designated here as BTG. The bulk BTG glass has the glass transition temperature of T_g=669, the crystallization onset temperature of T_x=809, and the crystallization peak temperature of T_p=838 °C.[10] As reported by Takahashi *et al.*,[3,4] the transparent BTG surface-crystallized glasses showing strong SHGs are obtained by heat treatment at 720 °C for 3 h. In this study, therefore, the BTG glass was crystallized with this heat treatment condition in the magnetic field of H=10 T. Furthermore, the three different kinds of BTG crystallized glasses obtained in this study are designated as follows; sample A is the crystallized glass obtained by heat treatment under the perpendicular application of H=10 T to the glass surface, sample B is the sample obtained by heat treatment under the parallel application of H=10 T to the glass surface, and sample C is the sample obtained by heat treatment in zero magnetic field, i.e., H=0 T. The XRD patterns for the bulk BTG crystallized glasses are shown in Fig. 1. The XRD peaks in these samples are assigned to the ferroelastic

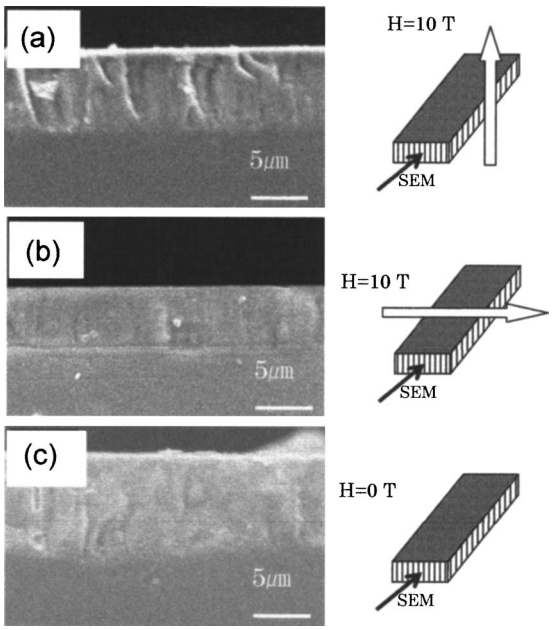

FIG. 2. SEM micrographs for the cross section of the crystallized glasses obtained by heat treatment at 720° C for 3 h in the magnetic field (H =10 T) and zero magnetic field (H=0 T).

$Ba_2TiGe_2O_8$ crystalline phase with an orthorhombic structure (space group: $Cmm2$),[3,4,16] indicating that $Ba_2TiGe_2O_8$ crystals are formed at the surface of the BTG glass even though the magnetic field of 10 T is applied during the crystallization. Furthermore, it is seen that the relative intensity of the peak corresponding to the (002) plane against the peaks for the (221) and (311) planes, $I(002)=I_{002}/(I_{221}+I_{311})$, changes depending on the applied direction of the magnetic field to the glass, i.e., I(200) for sample A $>I$(200) for sample C $>I$(200) for sample B. These data suggest that the c-axis orientation of the $Ba_2TiGe_2O_8$ crystals at the surface is enhanced or depressed depending on the applied direction of the magnetic field to the glass.

The SEM micrographs for the BTG crystallized glasses obtained by heat treatment at 720 °C for 3 h are shown in Fig. 2. The thickness of the $Ba_2TiGe_2O_8$ crystal layers at the surface is around 5–8 μm, and, in particular, sample B shows the thin crystalline layer compared with other two samples.

The Maker fringe patterns measured for the transparent BTG surface-crystallized glasses are shown in Fig. 3. In these measurements, to simplify the analysis of the Maker fringe patterns, one side of the sample surfaces consisting of the $Ba_2TiGe_2O_8$ crystals was mechanically eliminated, meaning that the crystalline layer presents only at one side of the sample.[3,4] The analysis of the experimental fringe patterns was carried out on the basis of the Maker fringe theory.[13,14] The Maker fringe pattern is generally described by the following equation;

$$P_{2\omega} = Cd_{\mathrm{eff}}^2 t_{\omega}'^4 T_{2\omega}'' R(\theta) P_{\omega}^2 \frac{\sin^2 \psi}{(n_{\omega}^2 - n_{2\omega}^2)^2}, \tag{2}$$

where $P_{2\omega}$ and P_{ω} are the intensities of SH wave and incident light, respectively. t_{ω}' and $T_{2\omega}''$ are the transmission factors of incident light and SH wave, respectively. $R(\theta)$ is the

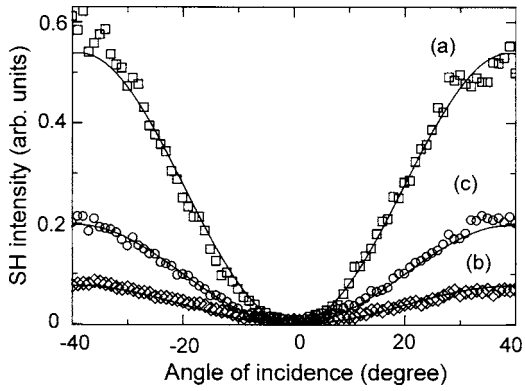

FIG. 3. Maker fringe patterns at room temperature for the transparent surface-crystallized glasses obtained by heat treatment at 720° C for 3 h in the magnetic field ($H=10$ T) and zero magnetic field ($H=0$ T). (a) The magnetic field applied during crystallization is perpendicular to the glass surface, (b) the magnetic field applied during crystallization is parallel to the glass surface, and (c) conventional crystallization in zero magnetic field.

multiple reflection correction, and n_ω and $n_{2\omega}$ are the refractive indices of incident light and SH wave, respectively. C is the constant related with laser beam area. ψ is defined by the following equation;

$$\psi = \frac{2\pi L}{\lambda}(n_\varpi \cos\theta'_\varpi - n_{2\varpi}\cos\theta'_{2\varpi}), \tag{3}$$

where L is the thickness of nonlinear medium, λ is the wavelength of the incident light, and θ'_ω and $\theta'_{2\omega}$ are the reflection angles of the incident light and SH wave, respectively. Furthermore, the equation of $d_{\text{eff}}=d_{33}\sin\theta_\omega$, which has been used for electrically poled glasses,[17] was adapted as the effective second-order optical nonlinear coefficient in this study.

The data shown in Fig. 3 were analyzed using Eqs. (2) and (3), in which the following values of n_ω, $n_{2\omega}$, and L were used: $n_\omega=1.80$, $n_{2\omega}=1.82$, and $L=8.69$ μm for sample A, $n_\omega=1.81$, $n_{2\omega}=1.84$, and $L=5.68$ μm for sample B, and $n_\omega=1.81$, $n_{2\omega}=1.83$, and $L=7.69$ μm for sample C. The theoretical Maker fringe patterns for these three samples are also shown in Fig. 3 (solid line). As a result of fitting, the d_{33} values were estimated to be 7.3 ± 0.5 pm/V for sample A, 3.7 ± 0.5 pm/V for sample B, and 5.6 ± 0.5 pm/V for sample C. It should be emphasized that the transparent surface-crystallized glass fabricated with the field perpendicular to the glass surface (sample A) shows the largest d_{33} value among these samples. Furthermore, the d_{33} value of sample B fabricated with the field parallel to the glass surface is smaller than that of sample C fabricated in zero magnetic field. We tried these experiments and analyses for several different samples and confirmed this tendency in the d_{33} values, i.e., d_{33} for sample A (perpendicular application of $H=10$ T to the glass surface) $>d_{33}$ for sample C ($H=0$ T) $>d_{33}$ for sample B (parallel application of $H=10$ T to the glass surface). The present study, therefore, indicates that the second-order optical nonlinearity of the transparent surface-crystallized glasses consisting of the $Ba_2TiGe_2O_8$ crystals is enhanced or depressed depending on the applied direction of the magnetic field (10 T).

It is known that in the fresnoite-type $Ba_2TiGe_2O_8$ crystals, corner-linked TiO_5 pentahedra and pyrogermanate groups Ge_2O_7 comprise flat sheets perpendicular to the [001] direction and these sheets are interconnected by tenfold-coordinated barium ions.[18,19] The most important feature relating to the spontaneous polarization in the fresnoite-type crystals is the presence of pyramidal TiO_5 units and their interconnections along the c axis, giving large polarizations along the c axis.[4,20] It is, therefore, expected that the SH intensity of crystallized glasses with $Ba_2TiGe_2O_8$ crystals would depend on the degree of c-axis orientations of $Ba_2TiGe_2O_8$ crystals. As shown in Fig. 1, the magnetic field of 10 T has the effect on the orientation of the $Ba_2TiGe_2O_8$ crystals at the surface of the crystallized glasses. The c-axis orientation in sample A is enhanced by the application of $H=10$ T, i.e., the c axis of the $Ba_2TiGe_2O_8$ crystals is parallel to the direction of the magnetic field and, indeed, the SH intensity in sample A is also enhanced. The present study, therefore, demonstrates that the growth behavior of the $Ba_2TiGe_2O_8$ crystals at the glass surface is affected by the application of the magnetic field of $H=10$ T during the crystallization.

Makiya *et al.*[7] and Suzuki and Sakka[21] reported that crystalline textures with c-axis orientations in the drying processing of a ferroelectric bismuth titanate slurry and in the slip casting processing of a titania slurry are developed by the parallel application of a high magnetic field ($H=10$ T) to the sample surface. These studies are not on the crystallization of glass but on the orientation of crystal particles with large crystallographic anisotropies in the liquidlike slurries. At this moment, there is no information on the anisotropy of paramagnetic susceptibilities in the structure of the $Ba_2TiGe_2O_8$ crystals. The present study, however, suggests that in the $Ba_2TiGe_2O_8$ crystals a magnetic anisotropy is present along the c-axis (i.e., along pyramidal TiO_5 units), consequently inducing the c-axis orientation at the surface when the magnetic field of $H=10$ T was applied perpendicularly to the surface plane of the BTG glass.

IV. CONCLUSION

We applied the magnetic field of $H=10$ T perpendicularly or parallel to the surface of the $30BaO.15TiO_2.55GeO_2$ (BTG) glass during its crystallization and examined the effect of the application of $H=10$ T on the crystal orientation and second-order optical nonlinearity of the $Ba_2TiGe_2O_8$ crystals formed at the glass surface. It was found that the c-axis orientation and second-harmonic intensity of the $Ba_2TiGe_2O_8$ crystals at the surface were enhanced in the sample fabricated with the field perpendicular to the surface and, by contrast, were depressed in the sample fabricated with the field parallel to the surface. The present study indicates that the application of high magnetic fields during crystallization is a technique to control the crystal orientations and optical properties of BTG crystallized glasses. It is desired to apply this technique to other crystallized glass systems.

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